

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C09D 5/44	A1	(11) International Publication Number: WO 00/64991 (43) International Publication Date: 02 November 2000 (02.11.2000)
(21) International Application Number: PCT/US00/09423 (22) International Filing Date: 07 April 2000 (07.04.2000) (30) Priority Data: 09/298,104 22 April 1999 (22.04.1999) US (60) Parent Application or Grant PPG INDUSTRIES OHIO, INC. [/]; O. KARABIN, Richard, F. [/]; O. KAYLO, Alan, J. [/]; O. UHL, William, J. ; O.	Published	
(54) Title: ELECTRODEPOSITION BATHS CONTAINING YTTRIUM (54) Titre: BAINS D'ELECTRODEPOSITION CONTENANT DE L'YTTRIUM (57) Abstract <p>Disclosed are improved electrodeposition bath compositions comprising a resinous phase dispersed in an aqueous medium, the resinous phase being comprised of an active hydrogen containing ionic electrodepositable resin and a curing agent, where the improvement comprises the addition to an electrodeposition bath of at least one source of yttrium in an amount of about 10 to 10,000 parts per million of total yttrium based on electrodeposition bath weight. The electrodeposition bath compositions are preferably cationic and provide for excellent corrosion resistance over a variety of metal substrates including untreated steel. Also disclosed is a method of electrocoating a conductive substrate using the improved electrodeposition bath compositions of the invention. Metallic substrates which are coated using the method of the invention are also disclosed.</p> (57) Abrégé <p>La présente invention concerne des compositions améliorées de bains d'électrodéposition comprenant une phase résineuse dispersée dans un milieu aqueux, la phase résineuse contenant une résine ionique à hydrogène actif, électrodéposable, et un agent de durcissement, l'amélioration portant sur l'addition, à un bain d'électrodéposition, d'au moins une source d'yttrium en une quantité d'environ 10 à 10000 parties par million d'yttrium total sur la base du poids du bain d'électrodéposition. Les compositions de bain d'électrodéposition sont de préférence cationiques et permettent d'obtenir une excellente résistance à la corrosion sur une variété de substrats métalliques, y compris l'acier non traité. L'invention concerne aussi un procédé d'électrodéposition sur un substrat conducteur au moyen des compositions de bains d'électrodéposition décrites. Elle concerne encore des substrats métalliques revêtus à l'aide du procédé décrit.</p>		

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09D 5/44	A1	(11) International Publication Number: WO 00/64991 (43) International Publication Date: 2 November 2000 (02.11.00)
(21) International Application Number: PCT/US00/09423 (22) International Filing Date: 7 April 2000 (07.04.00) (30) Priority Data: 09/298,104 22 April 1999 (22.04.99) US (71) Applicant: PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US). (72) Inventors: KARABIN, Richard, F.; RD #1, Box 461, Ruffs Dale, PA 15679 (US). KAYLO, Alan, J.; 140 Lingay Drive, Glenshaw, PA 15116 (US). (74) Agents: UHL, William, J.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>With amended claims.</i>	
(54) Title: ELECTRODEPOSITION BATHS CONTAINING YTTRIUM (57) Abstract Disclosed are improved electrodeposition bath compositions comprising a resinous phase dispersed in an aqueous medium, the resinous phase being comprised of an active hydrogen containing ionic electrodepositable resin and a curing agent, where the improvement comprises the addition to an electrodeposition bath of at least one source of yttrium in an amount of about 10 to 10,000 parts per million of total yttrium based on electrodeposition bath weight. The electrodeposition bath compositions are preferably cationic and provide for excellent corrosion resistance over a variety of metal substrates including untreated steel. Also disclosed is a method of electrocoating a conductive substrate using the improved electrodeposition bath compositions of the invention. Metallic substrates which are coated using the method of the invention are also disclosed.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Description

5

10

15

20

25

30

35

40

45

50

55

5

ELECTRODEPOSITION BATHS CONTAINING YTTRIUM

10

FIELD OF THE INVENTION

5 The present invention relates to improved coating compositions
and, in particular, to electrodeposition baths containing a resinous phase dispersed
15 in an aqueous medium, the resinous phase comprised of an ionic
electrodepositable resin, a curing agent therefor, a source of yttrium; and to their
use in the method of electrodeposition.

20

10

BACKGROUND OF THE INVENTION

 Electrodeposition as a coating application method involves
25 deposition of a film-forming composition onto a conductive substrate under the
influence of an applied electrical potential. Electrodeposition has become
15 increasingly important in the coatings industry because, by comparison with non-
electrophoretic coating means, electrodeposition offers increased paint utilization,
30 improved corrosion protection and low environmental contamination.

30

 Initially, electrodeposition was conducted with the workpiece
being coated serving as the anode. This was familiarly referred to as anionic
35 electrodeposition. However, in 1972, cationic electrodeposition was introduced
20 commercially. Since that time, cationic electrodeposition has steadily gained in
popularity and today is by far the most prevalent method of electrodeposition.
40 Throughout the world, more than 80 percent of all motor vehicles produced are
given a primer coating by cationic electrodeposition.

40

25 Typically, electrodepositable coatings comprise an
electrodepositable film-forming polymer and a curing agent, in combination with,
45 *inter alia*, pigments. Lead-containing pigments such as lead silica chromate, basic
lead silicate, lead chromate, and lead sulfate are often used in electrodepositable
coatings because they impart excellent corrosion resistance to the electrocoated

50

55

5 article. However, the acid used in cationic electrodeposition baths often
solubilizes a portion of the lead pigment forming lead salts which are soluble in
the aqueous phase of the electrodeposition bath. These lead salts often find their
10 way into the ultrafiltrate of the bath, thus necessitating the removal and
subsequent disposal of metallic lead and/or ionic or organic lead-containing
5 materials.

15 In recent years, due to environmental concerns, particularly in
Europe and Japan, the use of lead-free coatings has been mandated. Although
surface coatings of excellent quality can be achieved by means of cationic
10 electrodeposition of lead-free coatings, the removal of corrosion inhibitive lead
pigments can result in reduced corrosion resistance of these coatings, particularly
20 when applied to untreated or poorly pretreated steel substrates.

U.S. Patent No. 4,789,441 discloses a metallic coating on a
25 substrate applied by composite electrodeposition of a metallic matrix of nickel,
cobalt or iron which contains particles of CrAlM_2 where M_2 is yttrium, silicon, or
15 titanium. The composite electrodeposition metallic coating imparts corrosion
resistance to substrates which are used in aggressive media and is particularly
30 useful for coating gas turbine blades. This "coating" is completely metallic in
nature and must be fused with the substrate at temperatures of greater than 700°C ,
20 preferably over 1100°C in order to achieve diffusion of the deposited metals into
the substrate. Such coatings are unsuitable for general use in common industrial
35 painting applications.

The use of yttrium to improve corrosion resistance of
40 conventional organic coatings is not known in the art. Nor is the effectiveness of
yttrium as a corrosion inhibitor in conventional, cationic electrodepositable
25 coatings known. It, therefore, would be advantageous to provide a lead-free
electrodeposition bath containing a yttrium source which provides improved
45 corrosion resistance of the electrocoated metal substrates, especially untreated
steel.

5

SUMMARY OF THE INVENTION

10

In accordance with the present invention, a coating composition comprising (a) an active hydrogen group-containing resin and (b) a curing agent having functional groups reactive with the active hydrogen groups of (a). The composition contains yttrium or a compound of yttrium in an amount of about 0.005 to 5 percent, preferably not more than 2.5 percent, and more preferably not more than 1.0 percent by weight of yttrium (measured as elemental yttrium) based on weight of total resin solids.

15

In a particular embodiment, the invention resides in an electrodeposition bath, having improved corrosion resistance, comprising a resinous phase dispersed in an aqueous medium. The resinous phase comprises the following components:

20

25

- (a) an active hydrogen-group containing ionic electrodepositable resin, and
- (b) a curing agent having functional groups reactive with the active hydrogen groups of (a). Yttrium or a compound of yttrium is present in the electrodeposition bath in an amount from about 10 to about 10,000 parts per million of total yttrium (measured as elemental yttrium) based on electrodeposition bath weight.

30

Also provided is a method of electrocoating a conductive substrate serving as a charged electrode in an electrical circuit comprising the electrode and an oppositely charged counter electrode which are immersed in an aqueous electrodeposition bath described above, and metallic substrates coated by the method.

35

40

25

DETAILED DESCRIPTION OF THE INVENTION

Generally, the electrodeposition bath of the present invention comprises a resinous phase dispersed in an aqueous medium wherein the resinous phase comprises the following components:

45

- (a) an active hydrogen group-containing ionic electrodepositable resin, and
- (b) a curing agent having functional groups reactive with the active hydrogen groups of (a), wherein the improvement comprises an electrodeposition

30

50

55

5 bath containing yttrium present in an amount from about 10 to about 10,000 parts
per million, preferably not more than about 5,000 parts per million, and more
preferably not more than about 1,000 parts per million, of total yttrium (measured
10 as elemental yttrium).

5 At levels lower than 10 parts per million total yttrium, based on
electrodeposition bath weight, no appreciable improvement in corrosion resistance
of the electrocoated substrate is observed. At levels of yttrium greater than
15 10,000 ppm stability and application characteristics of the electrocoating bath
compositions can be negatively effected.

20 Both soluble and insoluble yttrium compounds may serve as the
source of yttrium in the electrodeposition baths of the invention. Examples of
yttrium sources suitable for use in the lead-free electrodeposition bath of the
present invention are soluble organic and inorganic yttrium salts such as yttrium
25 acetate, yttrium chloride, yttrium formate, yttrium carbonate, yttrium sulfamate,
15 yttrium lactate and yttrium nitrate. When the yttrium is to be added to an
electrocoat bath as an aqueous solution, yttrium nitrate, a readily available yttrium
compound, is a preferred yttrium source. Other yttrium compounds suitable for
30 use in the electrodeposition baths of the present invention are organic and
inorganic yttrium compounds such as yttrium oxide, yttrium bromide, yttrium
20 hydroxide, yttrium molybdate, yttrium sulfate, yttrium silicate, and yttrium
oxalate. Organoyttrium complexes and yttrium metal can also be used. When the
35 yttrium is to be incorporated into an electrocoat bath as a component in the
pigment paste, yttrium oxide is the preferred source of yttrium.

40 Besides the aforementioned yttrium compounds, the
25 electrodeposition baths of the present invention also contain, as a main film-
forming polymer, an active hydrogen-containing ionic, preferably cationic,
electrodepositable resin. A wide variety of electrodepositable film-forming
45 polymers are known and can be used in the electrodeposition baths of the
invention so long as the polymers are "water dispersible," i.e., adapted to be
30 solubilized, dispersed or emulsified in water. The water dispersible polymer is
50 ionic in nature, that is, the polymer will contain anionic functional groups to

5 impart a negative charge or, as is preferred, cationic functional groups to impart a positive charge.

10 Examples of film-forming resins suitable for use in anionic electrodeposition bath compositions are base-solubilized, carboxylic acid containing
5 polymers such as the reaction product or adduct of a drying oil or semi-drying fatty acid ester with a dicarboxylic acid or anhydride; and the reaction product of a fatty acid ester, unsaturated acid or anhydride and any additional unsaturated modifying
15 materials which are further reacted with polyol. Also suitable are the at least partially neutralized interpolymers of hydroxy-alkyl esters of unsaturated carboxylic
10 acids, unsaturated carboxylic acid and at least one other ethylenically unsaturated monomer. Still another suitable electrodepositable resin comprises an alkyd-aminoplast vehicle, i.e., a vehicle containing an alkyd resin
20 and an amine-aldehyde resin. Yet another anionic electrodepositable resin composition comprises mixed esters of a resinous polyol. These compositions are
25 described in detail in U.S. Pat. No. 3,749,657 at col. 9, lines 1 to 75 and col. 10, lines 1 to 13, all of which are herein incorporated by reference. Other acid
30 functional polymers can also be used such as phosphatized polyepoxide or phosphatized acrylic polymers as are well known to those skilled in the art.

As aforementioned, it is preferred that the active hydrogen-
20 containing ionic electrodepositable resin (a) is cationic and capable of deposition on a cathode. Examples of such cationic film-forming resins include amine salt
35 group-containing resins such as the acid-solubilized reaction products of polyepoxides and primary or secondary amines such as those described in U.S.
40 Pat. Nos. 3,663,389; 3,984,299; 3,947,338; and 3,947,339. Usually, these amine salt group-containing resins are used in combination with a blocked isocyanate
25 curing agent. The isocyanate can be fully blocked as described in the aforementioned U.S. Pat. No. 3,984,299 or the isocyanate can be partially blocked
45 and reacted with the resin backbone such as described in U.S. Pat. No. 3,947,338. Also, one-component compositions as described in U.S. Pat. No. 4,134,866 and
30 DE-OS No. 2,707,405 can be used as the film-forming resin. Besides the epoxy-

5 amine reaction products, film-forming resins can also be selected from cationic acrylic resins such as those described in U.S. Pat. Nos. 3,455,806 and 3,928,157.

10 Besides amine salt group-containing resins, quaternary ammonium salt group-containing resins can also be employed. Examples of these resins are
5 those which are formed from reacting an organic polyepoxide with a tertiary amine salt. Such resins are described in U.S. Pat. Nos. 3,962,165; 3,975,346; and
15 4,001,101. Examples of other cationic resins are ternary sulfonium salt group-containing resins and quaternary phosphonium salt-group containing resins such as those described in U.S. Pat. Nos. 3,793,278 and 3,984,922, respectively. Also,
20 film-forming resins which cure via transesterification such as described in European Application No. 12463 can be used. Further, cationic compositions prepared from Mannich bases such as described in U.S. Pat. No. 4,134,932 can be used.

25 The resins to which the present invention is particularly effective
15 are those positively charged resins which contain primary and/or secondary amine groups. Such resins are described in U.S. Pat. Nos. 3,663,389; 3,947,339; and
30 4,116,900. In U.S. Pat. No. 3,947,339, a polyketimine derivative of a polyamine such as diethylenetriamine or triethylenetetraamine is reacted with a polyepoxide. When the reaction product is neutralized with acid and dispersed in water, free
20 primary amine groups are generated. Also, equivalent products are formed when
35 polyepoxide is reacted with excess polyamines such as diethylenetriamine and triethylenetetraamine and the excess polyamine vacuum stripped from the reaction mixture. Such products are described in U.S. Pat. Nos. 3,663,389 and 4,116,900.

40 The active hydrogen-containing ionic electrodepositable resin
25 described above is present in the electrodeposition bath of the invention in amounts of about 1 to about 60 percent by weight, preferably about 5 to about 25 based on total weight of the electrodeposition bath.

45 The resinous phase of the electrodeposition bath of the present invention further comprises (b) a curing agent adapted to react with the active
30 hydrogen groups of the ionic electrodepositable resin (a) described immediately above. Both blocked organic polyisocyanate and aminoplast curing agents are
50

5 suitable for use in the present invention, although blocked isocyanates are preferred herein for cathodic electrodeposition.

10 Aminoplast resins, which are the preferred curing agent for anionic electrodeposition, are the condensation products of amines or amides with
5 aldehydes. Examples of suitable amine or amides are melamine, benzoguanamine, urea and similar compounds. Generally, the aldehyde employed is formaldehyde, although products can be made from other aldehydes such as
15 acetaldehyde and furfural. The condensation products contain methylol groups or similar alkylol groups depending on the particular aldehyde employed.
20 Preferably, these methylol groups are etherified by reaction with an alcohol. Various alcohols employed include monohydric alcohols containing from 1 to 4 carbon atoms such as methanol, ethanol, isopropanol, and n-butanol, with
25 methanol being preferred. Aminoplast resins are commercially available from American Cyanamid Co. under the trademark CYMEL and from Monsanto
15 Chemical Co. under the trademark RESIMENE.

The aminoplast curing agents are typically utilized in conjunction
30 with the active hydrogen containing anionic electrodepositable resin in amounts ranging from about 5 percent to about 60 percent by weight, preferably from about 20 percent to about 40 percent by weight, the percentages based on the total
20 weight of the resin solids in the electrodeposition bath.

35 The preferred curing agents for use in cathodic electrodeposition are blocked organic polyisocyanates. The polyisocyanates can be fully blocked as described in U. S. Patent No. 3,984,299 column 1 lines 1 to 68, column 2 and
40 column 3 lines 1 to 15, or partially blocked and reacted with the polymer backbone as described in U. S. Patent No. 3,947,338 column 2 lines 65 to 68,
25 column 3 and column 4 lines 1 to 30, which are incorporated by reference herein. By "blocked" is meant that the isocyanate groups have been reacted with a
45 compound so that the resultant blocked isocyanate group is stable to active hydrogens at ambient temperature but reactive with active hydrogens in the film
30 forming polymer at elevated temperatures usually between 90°C and 200°C.

5 Suitable polyisocyanates include aromatic and aliphatic
polyisocyanates, including cycloaliphatic polyisocyanates and representative
examples include diphenylmethane-4,4'-diisocyanate (MDI), 2,4- or 2,6-toluene
10 diisocyanate (TDI), including mixtures thereof, p-phenylene diisocyanate,
5 tetramethylene and hexamethylene diisocyanates, dicyclohexylmethane-4,4'-
diisocyanate, isophorone diisocyanate, mixtures of phenylmethane-4,4'-
15 diisocyanate and polymethylene polyphenylisocyanate. Higher polyisocyanates
such as triisocyanates can be used. An example would include triphenylmethane-
4,4',4"-triisocyanate. Isocyanate (-)-prepolymers with polyols such as neopentyl
10 glycol and trimethylolpropane and with polymeric polyols such as
20 polycaprolactone diols and triols (NCO/OH equivalent ratio greater than 1) can
also be used.

The polyisocyanate curing agents are typically utilized in
25 conjunction with the active hydrogen containing cationic electrodepositable resin
15 in amounts ranging from about 5 percent to about 60 percent by weight,
preferably from about 20 percent to about 50 percent by weight, the percentages
based on the total weight of the resin solids of the electrodeposition bath.

30 The aqueous compositions of the present invention are in the form
of an aqueous dispersion. The term "dispersion" is believed to be a two-phase
20 transparent, translucent or opaque resinous system in which the resin is in the
35 dispersed phase and the water is in the continuous phase. The average particle
size of the resinous phase is generally less than 1.0 and usually less than 0.5
microns, preferably less than 0.15 micron.

40 The concentration of the resinous phase in the aqueous medium is
25 at least 1 and usually from about 2 to about 60 percent by weight based on total
weight of the aqueous dispersion. When the compositions of the present
invention are in the form of resin concentrates, they generally have a resin solids
45 content of about 20 to about 60 percent by weight based on weight of the aqueous
dispersion.

30 Electrodeposition baths of the invention are typically supplied as
50 two components: (1) a clear resin feed, which includes generally the active

hydrogen-containing ionic electrodepositable resin, i.e., the main film-forming polymer, the curing agent, and any additional water-dispersible, non-pigmented components; and (2) a pigment paste, which generally includes one or more pigments, a water-dispersible grind resin which can be the same or different from the main-film forming polymer, and, optionally, additives such as wetting or dispersing aids. Electrodeposition bath components (1) and (2) are dispersed in an aqueous medium which comprises water and, usually, coalescing solvents.

It should be appreciated that there are various methods by which the yttrium compound can be incorporated into the electrodeposition bath. A soluble yttrium compound may be added "neat," that is, added directly to the bath without prior blending or reacting with other components. Alternatively, a soluble yttrium compound can be added to the predispersed clear resin feed which may include the ionic resin, the curing agent and/or any other non-pigmented component. Preferably, a soluble yttrium compound is added "neat" to the electrodeposition bath. Insoluble yttrium compounds and/or yttrium pigments, on the other hand, are preferably pre-blended with the pigment paste component prior to the incorporation of the paste to the electrodeposition bath.

The electrodeposition bath of the present invention can contain yttrium as the sole corrosion inhibiting inorganic component or can be supplemented with other corrosion inhibiting inorganic or organic components such as calcium, bismuth or polyphenols such as phenol functional polymers. Preferably the electrodeposition bath is substantially free of lead.

The electrodeposition bath of the present invention has a resin solids content usually within the range of about 5 to 25 percent by weight based on total weight of the electrodeposition bath.

As aforementioned, besides water, the aqueous medium may contain a coalescing solvent. Useful coalescing solvents include hydrocarbons, alcohols, esters, ethers and ketones. The preferred coalescing solvents include alcohols, polyols and ketones. Specific coalescing solvents include isopropanol, butanol, 2-ethylhexanol, isophorone, 2-methoxypentanone, ethylene and propylene glycol and the monoethyl, monobutyl and monohexyl ethers of

5 ethylene glycol. The amount of coalescing solvent is generally between about 0.01 and 25 percent and when used, preferably from about 0.05 to about 5 percent by weight based on total weight of the aqueous medium.

10 As discussed above, a pigment composition and, if desired, various additives such as surfactants, wetting agents or catalyst can be included in the dispersion. The pigment composition may be of the conventional type comprising pigments, for example, iron oxides, strontium chromate, carbon black, coal dust, 15 titanium dioxide, talc, barium sulfate, as well as color pigments such as cadmium yellow, cadmium red, chromium yellow and the like. The pigment content of the dispersion is usually expressed as a pigment-to-resin ratio. In the practice of the invention, when pigment is employed, the pigment-to-resin ratio is usually within the range of about 0.02 to 1:1. The other additives mentioned above are usually in the dispersion in amounts of about 0.01 to 3 percent by weight based on weight of resin solids.

15 The electrodepositable coating compositions of the present invention can be applied by electrodeposition to a variety of electroconductive substrates especially metals such as untreated steel, galvanized steel, aluminum, copper, magnesium and conductive carbon coated materials. The applied voltage for electrodeposition may be varied and can be, for example, as low as 1 volt to as 20 high as several thousand volts, but typically between 50 and 500 volts. The current density is usually between 0.5 ampere and 5 amperes per square foot and tends to decrease during electrodeposition indicating the formation of an insulating film.

40 After the coating has been applied by electrodeposition, it is cured usually by baking at elevated temperatures such as about 90° to about 260°C for about 1 to about 40 minutes.

45 Illustrating the invention are the following examples which, however, are not to be considered as limiting the invention to their details. All parts and percentages in the following examples as well as throughout the 50 specification are by weight unless otherwise indicated.

5

EXAMPLES

10

Examples A and B describe the preparation of cationic electrodepositable resins, Example A also containing a polyurethane crosslinker. Examples C and D each describe the preparation of quaternary ammonium salt containing pigment grinding resins.

15

Examples AA and BB describe the preparation of a pigment paste suitable for use in the electrodeposition bath compositions of the invention. Examples CC and DD describe the preparation of electrodeposition bath premixes for use in the electrodeposition bath compositions of Examples 1 and 2, and Examples 3 and 4, respectively. Example EE describes the preparation of the soluble yttrium solution for use in the bath compositions of Examples 2 and 4. Table 1 illustrates the improvement in scribe creep corrosion resistance observed with the inclusion of soluble yttrium solution in lead-free electrodeposition bath compositions of the invention.

25

15

EXAMPLE A

30

A polyurethane crosslinker was prepared from a mixture of the following ingredients:

35

INGREDIENTS	WEIGHT (grams)	EQUIVALENTS
<u>Charge I:</u>		
BPA/EO adduct ¹	2825.1	11.461
Ethanol	703	15.282
Propylene glycol	1161.4	---
Methyl isobutyl ketone	(15.282 moles)	---
	710.8	---
<u>Charge II:</u>		
PAPI 2940 ²	5042.9	38.204
Methyl isobutyl ketone	1249.5	---

45

¹ Adduct of Bisphenol A and a diol containing 6 ethylene oxide, commercially available as MACOL 98A MOD1 from BASF Corp.

50

² Polymeric methylene diphenyl diisocyanate available from The Dow Chemical Co.

55

Into a suitably equipped 12 liter round-bottom flask were added the ingredients of Charge I. Under mild agitation these ingredients were heated under a nitrogen blanket to a temperature of 50°C. The PAPI 2940 was added gradually over a period of about 2 hours with the temperature rising to 110°C, followed by a rinse of about 176.6 grams of the methyl isobutyl ketone. The reaction mixture was held at 110°C until no isocyanate was detected by infrared spectroscopy. The remaining 1072.7 grams of methyl isobutyl ketone was then added to the reaction mixture, which had a final solids content of about 83% (1 hour at 110°C).

A cationic resin was prepared from a mixture of the following ingredients:

INGREDIENTS	WEIGHT (grams)	EQUIVALENTS
<u>Charge I:</u>		
Polyurethane crosslinker as described immediately above	3658.1	
EPON 880 ¹	1971.6	10.487
Bisphenol A	760.4	6.7
BPA/EO adduct ²	2.5	0.005
TETRONIC 150R1 ³	0.6	---
Solvent ⁴	192.1	---
<u>Charge II:</u>		
Aminopropydiethanolamine ⁵	259.5	3.204
Diethanolamine	181.1	1.725
Benzyl dimethylamine	3.9	---

¹ Diglycidyl ether of Bisphenol A commercially available from Shell Oil and Chemical Co.

² Adduct prepared from 1:2 molar ratio of ethoxylated Bisphenol A (9 moles of ethylene oxide per mole of Bisphenol A) and hexahydrophthalic anhydride mixed in the presence of 0.05% triethylamine catalyst and held at 100°C for 3.5 hours.

³ Surfactant commercially available from BASF Corp.

⁴ Reaction product of 2 moles of diethylene glycol monobutyl ether and 1 mole formaldehyde, 98% active, prepared as described in U.S. Pat. No. 4,891,111 to McCollum et al.

⁵ Commercially available from Huntsman Corporation.

To a suitably equipped 12 liter round bottom flask were added the ingredients of Charge I. The reaction mixture was stirred under mild agitation and heated under a nitrogen blanket to a temperature of about 75°C, followed by the addition of Charge II. The reaction mixture was allowed to exotherm and after the exotherm had expired, the reaction temperature was adjusted to about 120° to 123°C and held at that temperature for about 2 hours. The reaction mixture had an epoxy equivalent weight of greater than 20,000 based on solids, an amine content of 0.77 milliequivalents per gram based on solids, and a Gardner-Holdt bubble viscosity of S/T (when reduced to 50% solids with 1-methoxy-2-propanol).

An aqueous dispersion of the cationic resin prepared above was prepared from a mixture of the following ingredients:

INGREDIENTS:	WEIGHT (grams)	EQUIVALENTS
<u>Charge I:</u>		
Sulfamic acid	155.1	1.597
Deionized water	4144.2	---
<u>Charge II:</u>		
Cationic resin prepared immediately above	6700.0	
<u>Charge III:</u>		
Gum rosin ¹	101.8	
<u>Charge IV:</u>		
Deionized water	4162.8	

¹ 30% solution of gum rosin (commercially available from Aldrich Chemical Company, Inc.) in methyl isobutyl ketone.

Charge I was added to a bath equipped with an agitator and heated to a temperature of 50°C. At this temperature, the cationic resin was added and mixed for about 30 minutes until thoroughly dispersed, at which time the gum rosin (Charge III) was gradually added. The cationic resin and gum rosin were mixed for 15 minutes, at which time the deionized water of Charge IV was added. The dispersion was heated to a temperature of about 60° to 65°C and subjected to a reduced pressure of about 20 inches mercury over a period of about 2 hours during which time the methyl isobutyl ketone was removed by vacuum distillation. The resulting dispersion had solids of 41.9% (1 hour at 110°C).

EXAMPLE B

A cationic resin was prepared from a mixture of the following ingredients:

INGREDIENTS:	WEIGHT (grams)	EQUIVALENTS
<u>Charge I:</u>		
EPON 880	376.0	2.000
Bisphenol A	148.0	1.300
BPA/EO adduct ¹	5.2	0.020
Solvent ²	59.6	
Ethyltriphenyl phosphonium iodide	0.53	
<u>Charge II:</u>		
Methylethanolamine	0.1	0.001
Diketimine ³	235.9	0.629

¹ Adduct of Bisphenol A and a diol containing 6 ethylene oxide, commercially available as MACOL 98A MOD1 from BASF Corp.

² Reaction product of 2 molcs of diethylene glycol monobutyl ether and 1 mole formaldehyde, 98% active, prepared as described in U.S. Pat. No. 4,891,111 to McCollum et al.

³ Diketimine derived from diethylene triamine and methyl isobutyl ketone (73% solids in methyl isobutyl ketone), prepared as described in U.S. Pat. No. 3,947,339 to Jerabek et al.

5 To a suitably equipped 5-liter flask the ingredients of Charge I
were added under mild agitation in the order shown above. The reaction mixture
10 was heated to a temperature of 125°C under a nitrogen blanket, then allowed to
exotherm to a temperature of about 145° to 160°C and subsequently held for one
5 hour at a temperature of about 145 °C. The reaction mixture was then cooled to a
temperature of about 125°C at which time the ingredients of Charge II were added
15 and the reaction mixture was held for two additional hours at that temperature.
After the hold period, approximately 85% of the reaction product was slowly
poured into an acetic acid solution (28.9 g (0.481 equivalents) and 190.0 grams
20 deionized water) and allowed to mix for 30 minutes. Additional deionized water
was added to reduce the dispersion solids to 36% (1 hour @ 110°C). The cationic
dispersion was then vacuum stripped to remove methyl isobutyl ketone.

25 EXAMPLE C

15 This example describes the preparation of a quaternary ammonium
salt containing pigment-grinding resin. Example C-1 describes the preparation of
an amine-acid salt quaternizing agent and Example C-2 describes the preparation
30 of an epoxy group-containing polymer that is subsequently quaternized with the
amine-acid salt of Example C-1.

35 EXAMPLE C-1

The amine-acid salt quaternizing agent was prepared using the
following procedure:

40 To a suitably equipped 5 liter flask were added 445 parts by weight
25 N, N-dimethylethanolamine. Under mild agitation, 660 parts by weight PAPI
2940 (polymeric diisocyanate commercially available from the Dow Chemical
Co.) were added slowly over a 1.5 hour period, followed by a rinse of 22.1 parts
45 by weight of the solvent mentioned above for Examples A and B. During this
addition, the reaction mixture was allowed to exotherm to a temperature of about
30 89°C and held at that temperature for about 1 hour until complete reaction of the
isocyanate as determined by infrared spectroscopy. At that time, 512 parts by

weight of an 88% aqueous lactic acid solution were added over a 25 minute period, followed by the addition of about 2136.11 parts by weight of deionized water. The reaction temperature was held at about 80°C for about 6 hours until a stalled acid value of 70.6 was obtained.

EXAMPLE C-2

The quaternary ammonium salt group-containing polymer was prepared using the following procedure.

To a suitably equipped 5 liter flask were added, under mild agitation, 528.8 parts by weight EPON 828 (polyglycidyl ether of Bisphenol A commercially available from Shell Oil and Chemical Co.); 224.9 parts by weight of Bisphenol A; 83.7 parts by weight of the solvent mentioned above in Examples A and B; and 0.5 parts by weight of ethyltriphenylphosphonium iodide. The reaction mixture was heated to about 140°C, allowed to exotherm to about 180°C, then cooled to about 160°C and held at that temperature for about 1 hour. At that time the polymeric product had an epoxy equivalent weight of 982.9. The reaction mixture was then cooled to a temperature of about 130°C at which time about 164.9 parts by weight of the solvent of Examples A and B was added and the temperature lowered to about 95°-100°C, followed by the addition of about 418.4 parts by weight of the amine-acid quaternizing agent of Example C-1 over a period of 15 minutes, and subsequently followed by the addition of about 1428.1 parts by weight of deionized water. The reaction temperature was held at about 80°C for approximately 6 hours until the acid number of the reaction product fell below 1.0. The resultant quaternary ammonium salt group-containing pigment grinding resin was further reduced with about 334.7 parts by weight of the solvent of Examples A and B.

EXAMPLE D

This example describes the preparation of a second quaternary ammonium salt group-containing pigment grinding resin. Example D-1 describes

5 the preparation of an amine-acid salt quaternizing agent and Example D-2
describes the preparation of an epoxy group-containing polymer that is
subsequently quaternized with the amine-acid salt of Example D-1.

5 **EXAMPLE D-1**

The amine-acid salt quaternizing agent was prepared using the
following procedure.

15 To a suitably equipped 5 liter flask were added under agitation
267.4 parts by weight N, N-dimethylethanolamine. At a temperature of about
23°C, 396 parts by weight of PAPI 2940 were slowly added over a 1.0 hour
20 period, followed by a rinse of about 13.9 parts by weight of the solvent mentioned
above in Examples A and B. The temperature was allowed to exotherm to about
90°C during this addition and was subsequently held at that temperature for about
45 minutes until the disappearance of the isocyanate as determined by infrared
25 spectroscopy. At that time, 112.8 parts by weight of dimethylcocoamine were
added followed by the addition of about 361.3 parts by weight of 88% aqueous
lactic acid solution over a 15-minute period. About 695.0 parts by weight of
deionized water were then added and the reaction temperature was held at about
85°C for about 3 hours until a stalled acid value was obtained.

20 **EXAMPLE D-2**

35 The quaternary ammonium salt group-containing polymer was
prepared using the following procedure.

40 To a suitably equipped 5 liter flask were added 631.7 parts by
weight EPON 828; 268.7 parts by weight Bisphenol A; 10.0 parts by weight of
25 the solvent of Examples A and B; and 0.6 parts of ethyltriphenylphosphonium
iodide. The reaction mixture was heated to about 140°C and allowed to exotherm
45 to a temperature of about 180°C at which time the reaction mixture was cooled to
160°C and held for about 1 hour to an epoxy equivalent weight of 991.0. The
30 reaction was further cooled to about 130°C and 421.2 parts by weight of
ethoxylated Bisphenol A (6 moles of ethylene oxide per mole of Bisphenol A)

5 were added. Cooling was then continued until a temperature of about 80°C was
obtained, at which time 346.4 parts by weight of the amine-acid salt quaternizing
agent of Example D-1 were added over a period of about 30 to 35 minutes,
10 followed by the addition of 404.8 parts by weight of deionized water. The
5 reaction mixture was held at a temperature of about 80°C for about 6 hours until
the acid number dropped below 1.0. The resultant quaternary ammonium salt
group-containing pigment grinding resin was further reduced with 2232.2 parts by
15 weight of deionized water.

20 EXAMPLE AA

This example describes the preparation of a pigment paste suitable
for use in the electrodeposition bath compositions of the present invention. The
pigment paste was prepared from a mixture of the following ingredients:

INGREDIENTS	WEIGHT (grams)
Quaternary ammonium salt group- containing grind resin of Example C	2002.4
Surfynol GA ¹	30.8
Deionized water	400
Ti-Pure R-900 ²	1725.0
CSX-333 ³	39.0
Catalyst paste ⁴	772.1
Deionized water	284.7

15 ¹ Nonionic surfactant available from Air Products and Chemicals, Inc.

² Titanium dioxide pigment available from E. I. DuPont de Nemours & Co. (Inc.)

³ Carbon black beads available from Cabot Corp.

⁴ Catalyst paste prepared from a mixture of the following ingredients:

5

10

15

INGREDIENTS	WEIGHT (grams)
Quaternary ammonium salt group-containing grind resin of Example D	632.0
Deionized water	92.0
n-Butoxypropanol	19.0
STANN BO ¹	368.0
¹ Di-n-butyltin oxide catalyst available from Sankyo Organic Chemicals Co., Ltd.	

20

The above ingredients were added, in the order shown, under high
shear agitation. After the ingredients were thoroughly blended, the pigment paste
was transferred to a vertical sand mill and ground to a Hegman value of about
7.25.

25

10

EXAMPLE BB

30

This example describes the preparation of a pigment paste suitable
for use in the electrodeposition bath compositions of the present invention. The
pigment paste was prepared from a mixture of the following ingredients:

35

40

45

50

INGREDIENTS	WEIGHT (grams)
Quaternary ammonium salt group- containing grind resin of Example C	2002.4
Surfynol GA ¹	30.8
Deionized water	400
Ti-Pure R-900 ²	1776.4
CSX-333 ³	39.9
Calcium oxalate hydrate ⁴	61.6
Catalyst paste ⁵	772.1
Deionized water	284.7

¹ Nonionic surfactant available from Air Products and Chemicals, Inc.

55

- ² Titanium dioxide pigment available from E. I. Dupont de Nemours & Co. (Inc.)
³ Carbon black beads available from Cabot Corp.
⁴ Calcium oxalate hydrate commercially available from Aldrich Chemical Company, Inc.
⁵ Catalyst paste prepared from a mixture of the following ingredients:

INGREDIENTS	WEIGHT (grams)
Quaternary ammonium salt group-containing grind resin of Example D	632.0
Deionized water	92.0
n-Butoxypropanol	19.0
STANN BO	368.0

The above ingredients were added sequentially under high shear agitation. After the ingredients were thoroughly blended, the pigment paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

EXAMPLE CC

This example describes the preparation of an electrodeposition bath premix for use in the electrodeposition bath compositions of Examples 1 and 2 below. The electrodeposition bath premix was prepared from a mixture of the following ingredients:

INGREDIENTS	WEIGHT (grams)
Cationic resin of Example A	3739.6
Cationic resin of Example B	226
Flexibilizer ¹	497
Flow additive ²	80
Solvent of Examples A and B	67.4
Pigment paste of Example AA	623.8
Phenylphosphonic acid ³	1.5
Deionized water	4764.7

¹ Reaction product of JEFFAMINE D400 (polyoxypropylenediamine available from Huntsman Corporation) and DER-732 (aliphatic epoxide commercially available from the Dow Chemical Co), prepared as described in U.S. Pat. No. 4,423,166 to Moriarity et al.

² Reaction product of methylamine; propylene oxide; and toluene diisocyanate as described in U.S. Pat. No. 5,348,578.

³ Phenylphosphonic acid commercially available from Aldrich Chemical Company, Inc.

EXAMPLE DD

This example describes the preparation of an electrodeposition bath premix for use in the electrodeposition bath compositions of Examples 3 and 4 below. The electrodeposition bath premix was prepared from a mixture of the following ingredients:

INGREDIENTS	WEIGHT(grams)
Cationic resin of Example A	3739.6
Cationic resin of Example B	226
Flexibilizer of Example CC	497
Flow additive of Example CC	80
Solvent of Examples A and B	67.4
Pigment paste of Example BB	623.8
Phenylphosphonic acid ¹	1.5
Deionized water	4764.7

¹ Phenylphosphonic acid commercially available from Aldrich Chemical Company, Inc.

EXAMPLE EE

This example describes the preparation of a soluble yttrium solution for use in the electrodeposition bath compositions of the Examples 2 and 4 below. The soluble yttrium solution was prepared from a mixture of the following ingredients:

INGREDIENTS	WEIGHT (grams)
Yttrium nitrate hexahydrate ¹	43.1
Deionized water	956.9

¹ Commercially available from Aldrich Chemical Company, Inc.

EXAMPLES 1 - 4

Examples 2 and 4 describe the preparation of electrodeposition bath compositions of the invention which contain 500 ppm of the soluble yttrium solution of Example EE. Comparative Examples 1 and 3 contain no soluble yttrium solution. The electrodeposition bath compositions were prepared from a mixture of the following ingredients:

	EXAMPLE 1 (Comparative)	EXAMPLE 2
ppm soluble yttrium:	0	500
Ingredients:	Weight (grams)	Weight (grams)
Premix of Example CC ultrafiltered 20%	2160	2160
Yttrium solution of Example EE	0.0	135
Deionized water	540	405

	EXAMPLE 3 (Comparative)	EXAMPLE 4
ppm soluble yttrium:	0	500
Ingredients:	Weight (grams)	Weight (grams)
Premix of Example DD ultrafiltered 20%	2160	2160
Yttrium solution of Example EE	0.0	135
Deionized water	540	405

ELECTRODEPOSITION BATH PREPARATION:

Under agitation, the cationic resin of Example B was diluted with approximately 15% of the total deionized water. The diluted resin was then stirred into the cationic resin of Example A. The flexibilizer resin was separately diluted with the solvent under agitation, then further diluted with about 30% of the total deionized water before adding to the cationic resin blend. The flow control additive was then added. The phenylphosphonic acid was diluted with about 5% of the total deionized water before adding to the cationic resin blend. The pigment

paste was separately diluted with the remaining deionized water and added to the above resin blend. Final bath solids were about 22.5%, with a pigment to resin ratio of 0.12:1.0. The test baths were 20% ultrafiltered and replenished with only fresh deionized water for Comparative Examples 1 and 3, and with fresh deionized water and the prescribed amount of soluble yttrium solution in Examples 2 and 4 prior to electrocoating.

ELECTROCOATING PROCEDURE:

Each of the electrodeposition bath compositions of Examples 1 through 4 above were electrodeposited onto non-phosphated cold rolled steel panels, commercially available from ACT Laboratories. Conditions for cationic electrodeposition of each were as follows: 2 minutes at 90°F at 160-180 volts to yield a cured film thickness of 0.6 to 0.8 mils. The coated substrate was cured in an electric oven at 340°F for 20 minutes.

TESTING PROCEDURE:

Each of the coated untreated steel test panels was scribed, cutting through the coating to the metal substrate, in an "X" pattern. The test panels were then subjected to salt spray testing in accordance with ASTM B117. Test panels were evaluated for "scribe creep" corrosion and visual appearance. Scribe creep is reported as average distance (in millimeters) of corrosion from the scribe mark. Test results are reported in the following TABLE 1.

TABLE 1

EXAMPLE	1	2	3	4
Soluble yttrium	0 ppm	500 ppm	0 ppm	500 ppm
Scribe Creep (mm)	12	7	10	5

The data reported in the above TABLE 1 illustrates the improvement in scribe creep corrosion resistance observed with the inclusion of soluble yttrium solutions in the electrodeposition baths of the invention.

Claims

5

10

15

20

25

30

35

40

45

50

55

5

WE CLAIM:

10

1. In an electrodepositable coating composition, said coating composition comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising:

15

(a) an active hydrogen group-containing ionic electrodepositable resin, and

(b) a curing agent having functional groups reactive with the active hydrogen groups of (a),

20

- the improvement comprising the inclusion in the composition of at least one source of yttrium present in an amount from about .005 percent by weight to about 5 percent by weight of yttrium based on weight of total resin solids of the electrodepositable coating composition.

25

2. The electrodepositable coating composition of claim 1 wherein the amount of yttrium present is not more than about 1.0 percent by weight based on weight of total resin solids in the electrodepositable coating composition.

30

3. The electrodepositable coating composition of claim 1 wherein said composition is substantially free of lead.

35

4. The electrodepositable coating composition of claim 1 wherein said resinous phase further comprises at least one non-lead pigment.

40

5. The electrodepositable coating composition of claim 1 wherein said yttrium source is a yttrium compound selected from the group consisting of yttrium oxide, yttrium nitrate, yttrium acetate, yttrium chloride, yttrium sulfamate, yttrium lactate, yttrium formate and mixtures thereof.

45

6. The electrodepositable coating composition of claim 5 wherein said yttrium compound is yttrium oxide.

50

55

5

10

7. The electrodepositable coating composition of claim 1 wherein said yttrium compound is a soluble salt of yttrium selected from the group consisting of yttrium sulfamate, yttrium acetate, yttrium lactate, yttrium formate and yttrium nitrate.

5

15

8. The electrodepositable coating composition of claim 1 wherein said active hydrogen containing ionic resin is cationic.

20

9. In an electrodeposition bath, said electrodeposition bath comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising:

(a) an active hydrogen group-containing ionic electrodepositable resin,

and

25

(b) a curing agent having functional groups reactive with the active hydrogen groups of (a),

15

the improvement comprising an electrodeposition bath containing at least one source of yttrium present in an amount from about 10 parts per million to about 10,000 parts per million of yttrium, based on electrodeposition bath weight.

30

35

10. The electrodeposition bath of claim 9 wherein the amount of yttrium is not more than about 1000 parts per million based on electrodeposition bath weight.

40

11. The electrodeposition bath of claim 9 wherein said bath is substantially free of lead.

25

45

12. The electrodeposition bath of claim 9 wherein said resinous phase further comprises at least one non-lead pigment.

50

13. The electrodeposition bath of claim 9 wherein said yttrium source is a yttrium compound selected from the group consisting of yttrium oxide, yttrium

55

5 nitrate, yttrium acetate, yttrium chloride, yttrium sulfamate, yttrium lactate,
yttrium formate and mixtures thereof.

10 14. The electrodeposition bath of claim 13 wherein said yttrium compound
5 is yttrium oxide.

15 15. The electrodeposition bath of claim 9 wherein said yttrium compound
is a soluble salt of yttrium selected from the group consisting of yttrium
sulfamate, yttrium acetate, yttrium lactate, yttrium formate and yttrium nitrate.

10 16. The electrodeposition bath of claim 9 wherein said active hydrogen
20 group-containing ionic resin is cationic.

25 17. A coating composition containing the following components:

- 15 (a) an active hydrogen group-containing resin; and
(b) a curing agent having functional groups reactive with the
active hydrogen groups of (a),

30 wherein the coating composition comprises about .005 percent by weight
to about 5.0 percent by weight of yttrium based on weight of total resin solids in
20 the coating composition.

35 18. A method of electrocoating a conductive substrate serving as a
charged electrode in an electrical circuit comprising said electrode and an
40 oppositely charged counter electrode, said electrodes being immersed in an
25 aqueous electrocoating composition, comprising passing electric current between
said electrodes to cause deposition of the electrocoating composition on the
substrate as a substantially continuous film, the aqueous electrocoating
45 composition comprising:

- 30 (a) an active hydrogen group-containing ionic electrodepositable resin, and
(b) a curing agent having functional groups reactive with the active
50 hydrogen groups of (a),

5

wherein the improvement comprises an electrodeposition bath containing at least one yttrium compound present in an amount from about 10 parts per million to about 10,000 parts per million of total, based on electrodeposition bath weight.

10

5

19. The method of claim 18 wherein the amount of yttrium is not more than about 1,000 parts per million based on electrodeposition bath weight.

15

20. The method of claim 18 wherein the amount of total yttrium is not more than about 500 parts per million, based on electrodeposition bath weight.

20

21. The method of claim 18 wherein the electrodeposition bath is substantially free of lead.

25

22. The method of claim 18 wherein said resinous phase further comprises at least one non-lead pigment.

30

23. The method of claim 18 wherein said yttrium compound is a soluble salt of yttrium selected from the group consisting of yttrium sulfamate, yttrium acetate, yttrium lactate, yttrium formate and yttrium nitrate.

35

24. The method of claim 18 wherein said yttrium compound is yttrium oxide.

40

25. The method of claim 18 wherein the substrate is the cathode.

25

26. The method of claim 18 wherein said substrate is comprised of untreated steel.

45

27. The method of claim 18 wherein said substrate is comprised of galvanized steel.

50

55

5

28. The method of claim 18 wherein said substrate is comprised of
aluminum.

10

5 29. An untreated steel substrate coated by the method of claim 26.

15

30. A galvanized steel substrate coated by the method of claim 27.

31. An aluminum substrate coated by the method of claim 28.

10

20

25

30

35

40

45

50

55

AMENDED CLAIMS

[received by the International Bureau on 13 September 2000 (13.09.00);
original claims 1, 9, 13 – 16, 18 and 19 amended;
remaining claims unchanged (4 pages)]

1. In an electrodepositable coating composition, said coating composition comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising:

(a) an active hydrogen group-containing ionic electrodepositable resin.
and

(b) a curing agent having functional groups reactive with the active hydrogen groups of (a).

the improvement comprising the inclusion in the composition of at least one source of soluble yttrium present in an amount from about .005 percent by weight to about 5 percent by weight of yttrium based on weight of total resin solids of the electrodepositable coating composition.

2. The electrodepositable coating composition of claim 1 wherein the amount of yttrium present is not more than about 1.0 percent by weight based on weight of total resin solids in the electrodepositable coating composition.

3. The electrodepositable coating composition of claim 1 wherein said composition is substantially free of lead.

4. The electrodepositable coating composition of claim 1 wherein said resinous phase further comprises at least one non-lead pigment.

5. The electrodepositable coating composition of claim 1 wherein said yttrium source is a yttrium compound selected from the group consisting of yttrium oxide, yttrium nitrate, yttrium acetate, yttrium chloride, yttrium sulfamate, yttrium lactate, yttrium formate and mixtures thereof.

6. The electrodepositable coating composition of claim 5 wherein said yttrium compound is yttrium oxide.

5

10

7. The electrodepositable coating composition of claim 1 wherein said yttrium compound is a soluble salt of yttrium selected from the group consisting of yttrium sulfamate, yttrium acetate, yttrium lactate, yttrium formate and yttrium nitrate.

5

15

8. The electrodepositable coating composition of claim 1 wherein said active hydrogen containing ionic resin is cationic.

20

9. In an electrodeposition bath, said electrodeposition bath comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising:
(a) an active hydrogen group-containing ionic electrodepositable resin,
and

25

(b) a curing agent having functional groups reactive with the active hydrogen groups of (a),
the improvement comprising an electrodeposition bath containing at least one source of soluble yttrium present in an amount from about 10 parts per million to about 10,000 parts per million of yttrium, based on electrodeposition bath weight.

30

35

10. The electrodeposition bath of claim 9 wherein the amount of yttrium is not more than about 1000 parts per million based on electrodeposition bath weight.

40

11. The electrodeposition bath of claim 9 wherein said bath is substantially free of lead.

45

12. The electrodeposition bath of claim 9 wherein said resinous phase further comprises at least one non-lead pigment.

50

13. The electrodeposition bath of claim 9 wherein said yttrium source is a yttrium compound selected from the group consisting of yttrium oxide, yttrium

55

5 nitrate, yttrium acetate, yttrium chloride, yttrium sulfamate, yttrium lactate,
yttrium formate and mixtures thereof.

10 14. The electrodeposition bath of claim 13 wherein said yttrium compound
5 is yttrium oxide.

15 15. The electrodeposition bath of claim 9 wherein said yttrium compound
is a soluble salt of yttrium selected from the group consisting of yttrium
sulfamate, yttrium acetate, yttrium lactate, yttrium formate and yttrium nitrate.

10

20 16. The electrodeposition bath of claim 9 wherein said active hydrogen
group-containing ionic resin is cationic.

25 17. A coating composition containing the following components:

25

15

(a) an active hydrogen group-containing resin; and

(b) a curing agent having functional groups reactive with the
active hydrogen groups of (a),

30

wherein the coating composition comprises about .005 percent by weight
to about 5.0 percent by weight of yttrium based on weight of total resin solids in
20 the coating composition.

35

18. A method of electrocoating a conductive substrate serving as a
charged electrode in an electrical circuit comprising said electrode and an
oppositely charged counter electrode, said electrodes being immersed in an
40 25 aqueous electrocoating composition, comprising passing electric current between
said electrodes to cause deposition of the electrocoating composition on the
substrate as a substantially continuous film, the aqueous electrocoating
composition comprising:

45

30

(a) an active hydrogen group-containing ionic electrodepositable resin,

and

(b) a curing agent having functional groups reactive with the active
hydrogen groups of (a),

50

55

5

10

wherein the improvement comprises an electrodeposition bath containing at least one source of soluble yttrium present in an amount from about 10 parts per million to about 10,000 parts per million of total yttrium, based on electrodeposition bath weight.

5

15

19. The method of claim 18 wherein the amount of total yttrium is not more than about 1,000 parts per million based on electrodeposition bath weight.

20

20. The method of claim 18 wherein the amount of total yttrium is not more than about 500 parts per million, based on electrodeposition bath weight.

25

21. The method of claim 18 wherein the electrodeposition bath is substantially free of lead.

15

22. The method of claim 18 wherein said resinous phase further comprises at least one non-lead pigment.

30

23. The method of claim 18 wherein said yttrium compound is a soluble salt of yttrium selected from the group consisting of yttrium sulfamate, yttrium acetate, yttrium lactate, yttrium formate and yttrium nitrate.

35

24. The method of claim 18 wherein said yttrium compound is yttrium oxide.

40

25. The method of claim 18 wherein the substrate is the cathode.

45

26. The method of claim 18 wherein said substrate is comprised of untreated steel.

30

27. The method of claim 18 wherein said substrate is comprised of galvanized steel.

50

55

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 00/09423

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09D5/44

According to International Patent Classification (IPC) or to national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 554 023 A (CIBA GEIGY AG) 4 August 1993 (1993-08-04) page 3, line 18 - line 44 page 4, line 31 - line 35 page 6, line 45 - line 51 page 7, line 19 - line 41 ---	1-4,8,17
P,X	CHEMICAL ABSTRACTS, vol. 132, Columbus, Ohio, US; abstract no. 182100. OKUMURA, YOSHIKI ET AL: "Cathodic electrodeposition coating compositions with good corrosion resistance" XP002143478 abstract & JP 2000 063710 A (NIPPON PAINT CO., LTD., JAPAN) 29 February 2000 (2000-02-29) --- -/-	1-5, 7-13, 15-23, 25,26,29

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "S" document member of the same patent family

Date of the actual completion of the international search:

26 July 2000

Date of mailing of the international search report:

08/08/2000

Name and mailing address of the ISA:

European Patent Office, P.B. 5816 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx: 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer:

Schlicke, B

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/09423

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 5 582 704 A (FAUCHER PHILIPPE ET AL) 10 December 1996 (1996-12-10) column 1, line 50 -column 2, line 6 claim 1 example 2</p> <p>-----</p>	1-31

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. J. Appl. No.
PCT/US 00/09423

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0554023 A	04-08-1993	AT 152160 T	15-05-1997
		AU 660210 B	15-06-1995
		AU 3198493 A	29-07-1993
		CA 2087895 A	26-07-1993
		DE 69309976 D	28-05-1997
		DE 69309976 T	27-11-1997
		JP 6080906 A	22-03-1994
		US 5250325 A	05-10-1993
JP 2000063710 A	29-02-2000	NONE	
US 5582704 A	10-12-1996	AT 182353 T	15-08-1999
		AU 691046 B	07-05-1998
		AU 3891895 A	31-05-1996
		CA 2204434 A	17-05-1996
		CN 1167497 A	10-12-1997
		DE 69510951 D	26-08-1999
		DE 69510951 T	30-03-2000
		EP 0789732 A	20-08-1997
		ES 2136884 T	01-12-1999
		JP 10500172 T	06-01-1998
		TR 960389 A	21-06-1996
		WO 9614363 A	17-05-1996
		US 5760107 A	02-06-1998